Stabilised Enamine Anions. Generation and Alkylation of Anions stabilised as Cyclopentadienide Enamine Systems †

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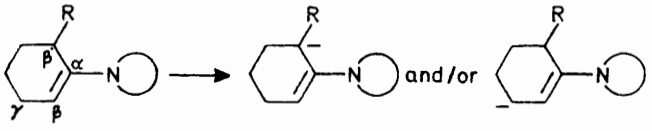
Pyrrolidine enamines from indan-1-one, indan-2-one, and 3,4-diphenylcyclopent-2-enone were converted into the corresponding anions (3), (14), and (23) by treatment with n-butyl-lithium in tetrahydrofuran at −65 to 25 °C. Treatment of the anion (3) with methyl iodide provided a methylated enamine which was (*a*) hydrolysed to 3-methylindan-1-one (82%), (*b*) subjected to a second anionic methylation to give 3,3-dimethylindan-1-one (95%), and (*c*) acylated to give 2-benzoyl-3-methylindan-1-one (19%). Corresponding treatment of the anion (14) produced (*a*) 1-methylindan-2-one (68%), (*b*) a mixture of dimethylated products (84%), and (*c*) 3-benzoyl-1-methyl-2-(pyrrolidin-1-yl)indene (51%). Corresponding treatment of the anion (23) gave (*a*)2-methyl-3,4-diphenylcyclopent-2-enone (51%) and (*b*) 5-acetyl-2-methyl-3,4-diphenylcyclopent-2-enone (15%).

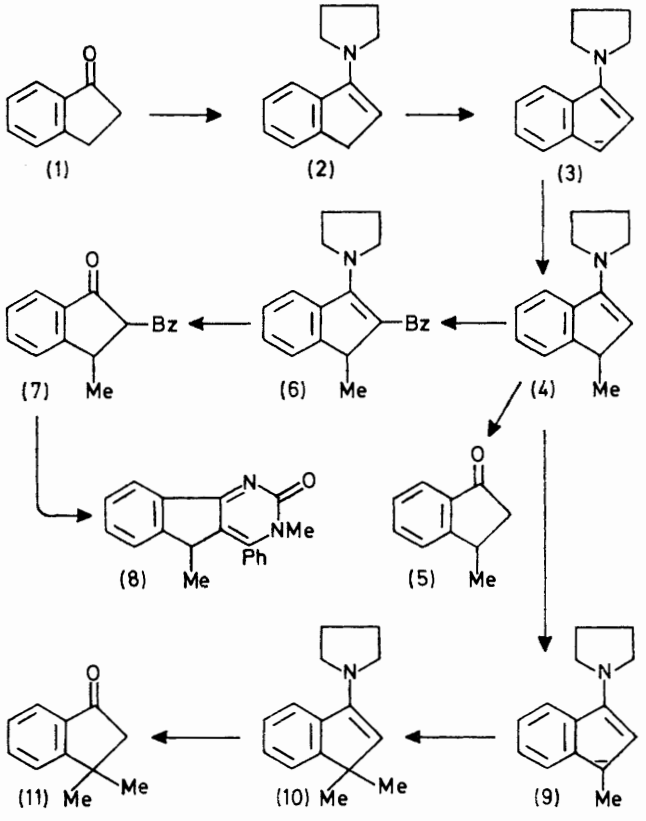
THE many factors affecting relative stabilities of the isomeric enamines formed from simple unsymmetrical ketones appear often to be delicately balanced. The resulting low degree of regioselectivity in formation of some enamines under equilibrium conditions [1-4] has consequences in subsequent steps, where mixtures of products may be obtained.[2,4] If it were possible to deprotonate an enamine by removing a β′-allylic hydrogen, the result would be conversion of isomeric enamines back into a single reactive species, which might (but would not necessarily) lead to a single product in substitution reactions.

Use of n.m.r. shifts as a rough index of electron density suggests that, while an enamine's β-carbon atom is appreciably more electron-rich than in simple olefins,[3] the α-carbon atom is slightly electron-depleted.‡ Therefore, in the absence of other factors, deprotonation in the above sense seems more likely than removal of a γ-hydrogen atom to produce a linearly conjugated anion. However in enamines, such as those of phenones, which lack a β′-allylic hydrogen, only a γ-anion could be formed (see Scheme 1).



SCHEME 1

We undertook to explore some of the possibilities of such reactions; however our preliminary investigation of several enamines suggested that, even with very powerful bases, in order to render a β′- or γ-allylic proton acidic to an extent useful for anion formation, appreciable stabilisation other than that provided by the enamine itself would be necessary. The carbonyl group has already been shown capable of stabilising an enamine anion to a synthetically useful degree.[5] Another system fulfilling these criteria is a cyclopentadienide system, which generally confers anion stability at least equal to and in some instances appreciably greater than that in



SCHEME 2

monocarbonyl compounds.[6] Enamines from both indan-1-one and indan-2-one have been reported,[7,8] and are

† Preliminary communication, H. W. Thompson and B. S. Huegi, *J.C.S. Chem. Comm.*, 1973, 636.

‡ α-Deprotonation of *NN*-dimethylvinylamine by n-butyl-lithium–tetramethylethylenediamine has recently been achieved (R. B. Bates, W. A. Beavers, and I. R. Blacksburg, Div. of Org. Chem. Abstract No. 16, 169th Amer. Chem. Soc. Meeting, April 1975).

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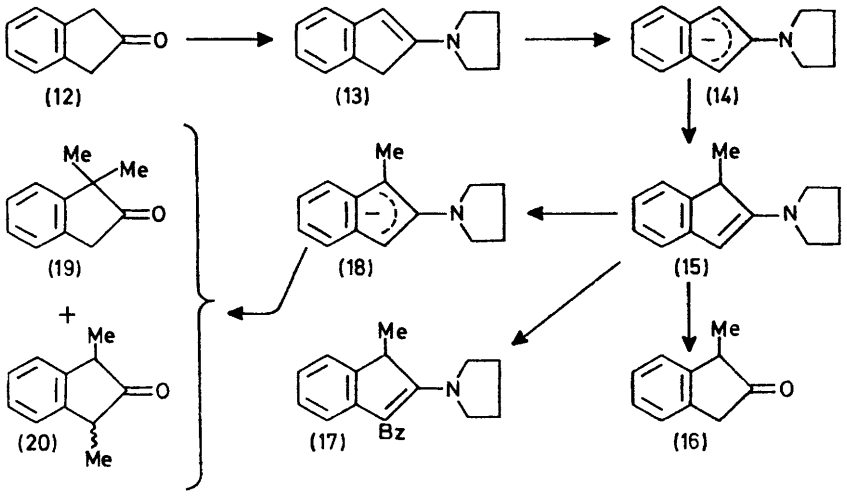
readily formed by the simpler preparative methods. We have examined such enamines, as well as one derived from a stabilised cyclopentenone, and have found that reactive anions are easily formed with strong base and a second portion of methyl iodide. Hydrolysis afforded the known 3,3-dimethylindan-1-one (11), isolated in 95% yield (and of high purity).

The pyrrolidine enamine (13) from indan-2-one [8] was



SCHEME 3

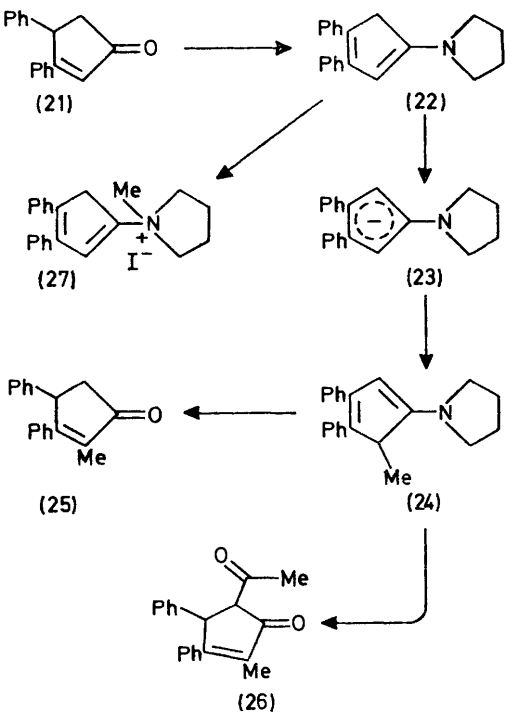
can be alkylated in high yields; the alkylation products can be converted into geminally, vicinally, or 1,3-disubstituted compounds by further reaction.

When the pyrrolidine enamine (2) from indan-1-one [7] was treated in tetrahydrofuran at −65 °C with 1.2 equiv. of n-butyl-lithium the anion (3) was formed, as indicated by evolution of gas on warming and formation of a yellow solution. Quenching this solution with 1.2 equiv. of methyl iodide resulted in immediate decolourisation, and 3-methylindan-1-one (5) (82%) was isolated. The possibility that this product was 2-methylindanone, which might arise by normal alkylation of the uncharged enamine, was eliminated by subsequent transformations and by comparison of the known derivatives and n.m.r. spectral data of these two compounds, establishing that the product is indeed derived from the allylic anion (3). Like (2), the methylated enamine (4) is isolable but soon deteriorates even when kept at 0 °C under nitrogen. Further reactions of (4) were therefore performed without its isolation.

That (4) is a normal enamine capable of the usual reactions was demonstrated by room-temperature acylation with benzoyl chloride and triethylamine, giving the benzoylated material (7). Conversion of (7) into the *N*-methylpyrimidone (8), which retains a methyl doublet in the n.m.r. spectrum, further demonstrated that alkylation had taken place at the 3- as opposed to the 2-position. The structure of (8), involving methyl substitution on N-3 rather than on N-1, was established by single-crystal *X*-ray analysis.* 3,3-Dialkylation was achieved by treatment of (4) with a second portion of butyl-lithium in refluxing tetrahydrofuran, followed by

* This analysis, carried out with a Syntex model $P2_1$ automatic *X*-ray diffractometer, was performed by Professor R. A. Lalancette and Mr. W. F. Furey, of this Department, whom we thank.

similarly capable of deprotonation by treatment with n-butyl-lithium at −65 °C in tetrahydrofuran. The reddish-brown solution of the anion (14) was decolourised



SCHEME 4

by addition of methyl iodide, and the resultant substituted enamine provided, on hydrolysis, a 68% yield of 1-methylindan-2-one (16) of high purity. This yield is higher than those reported for direct alkylation of the uncharged enamines of (12), which in the most favourable

cases did not exceed 40%.[8] Sequential 1,3-reaction of the 2-(pyrrolidin-1-yl)indene anion with methyl iodide and then benzoyl chloride–triethylamine for 18 h at 25 °C gave a 51% yield of methylated benzoylenamine (17). Our attempt at sequential anionic dialkylation of the enamine (13) led to an 84% yield (after distillation) of a mixture with three principal alkylated components, whose n.m.r. spectrum, consistent with a mixture of 1,1- and 1,3-dimethylindan-2-ones [(19) and (20)] suggested a lack of regiospecificity in the second alkylation.

Although unsubstituted cyclopentadiene undergoes rapid Diels–Alder self-condensation, we anticipated that the phenyl substituents on 3,4-diphenylcyclopent-2-enone (21) would not only stabilise the corresponding enamine but render formation of an anion particularly easy. This material was readily converted into the pyrrolidine enamine, which possessed the completely conjugated structure (22), according to its n.m.r. spectrum. Treatment as before gave the coloured solution of the anion (23), which provided the crystalline methylcyclopentenone (25) in 51% yield after purification. By contrast, in an attempt to methylate (21) *via* the uncharged enamine (22), we isolated only the quaternary *N*-alkylation product (27). A 1,3-alkylation–acylation sequence provided low yields of (isolated) 5-acetyl-2-methyl-3,4-diphenylcyclopent-2-enone (26) and the 2-methylated material (25).

EXPERIMENTAL

M.p.s were determined with a Mel-Temp apparatus. I.r. spectra were taken with a Beckman IR-10 spectrometer and CCl_4 or $CHCl_3$ as solvent unless otherwise noted. N.m.r. spectra were taken with a Varian A-60 or T-60 spectrometer, with CCl_4 or $CDCl_3$ as solvent and Me_4Si as internal standard. G.l.c. analyses were carried out with a Hewlett-Packard 5750 instrument with a flame-ionisation detector and a 0.125 in × 6 ft stainless steel column packed with 10% UC-W98 silicone on 80—100 mesh firebrick. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois, and through the courtesy of Sandoz-Wander Inc., Hanover, New Jersey.

3-(*Pyrrolidin*-1-*yl*)*indene* (2).—A mixture of indan-1-one (10 g, 76 mmol), pyrrolidine (8.0 ml, 96 mmol), and toluene-*p*-sulphonic acid (50 mg) was refluxed under nitrogen in benzene (100 ml) with azeotropic water separation (*ca.* 18 h usually required). Vacuum concentration and two Vigreux distillations gave the enamine (2) (8.7 g, 62%) as an unstable oil, b.p. 116—119° at 0.08 mmHg (lit.,[7] 142—144° at 2 mmHg); δ 1.9 (4 H, m), 3.35 (6 H, complex), 5.0 (1 H, t, *J* 2.5 Hz), and 7.05—7.75 (4 H, complex).

3-*Methylindan*-1-*one* (5).—A solution of the enamine (2) (3.0 g, 16.2 mmol; freshly distilled) in dry tetrahydrofuran (THF) (40 ml) under nitrogen was cooled to *ca.* −65 °C. Addition of n-butyl lithium (1.6M in hexane; 12 ml, 19.2 mmol) in small portions with stirring was followed by stirring for 15—20 min at −65 °C (a clear bright yellow solution was formed within minutes). The solution of the anion (3) was then quenched with methyl iodide (1.2 ml, 19 mmol), with an immediate colour change to blue-violet and slower precipitation of white solid. After 5 min stirring, the cooling bath was removed and the temperature was raised to 25 °C before addition of aqueous 10% ammonium chloride (20 ml). The resulting blue solution was stirred for 1 h at 25 °C under nitrogen, then more water (10 ml) was added and THF was removed *in vacuo*. The remaining aqueous mixture was worked up as usual, dried, decolourised, and concentrated to give nearly pure material (2.15 g), which was distilled to furnish the ketone (5) (1.95 g, 82%) as a liquid, b.p. 71—74° at 0.4 mmHg (lit.,[9] 120° at 8 mmHg); $\nu_{max.}$ 1 710 cm^{-1}; δ 1.35 (3 H, d, *J* 7 Hz), 2.15 (1 H, dd, *J* 4 and 19), 2.8 (1 H, dd, *J* 7 and 19), 3.4 (1 H, sym. decet, *J* 4 and 7), and 7.15—7.8 (4 H complex) [10] [no indan-1-one (1) signals were detected]. The 2,4-dinitrophenylhydrazone, prepared in 92% yield, had m.p. 234.5—236° (from THF–Et_2O) (lit.,[9,11] 240°; *cf.* lit.,[12] m.p. 201—203° for the 2-methylindanone derivative) (Found: C, 58.8; H, 4.3. Calc. for $C_{16}H_{14}N_4O_4$: C, 58.9; H, 4.3%).

In a similar preparation involving 1.0 g of the enamine (2), the hydrolysis step was replaced by vacuum concentration and distillation of the residue to afford the enamine (4) (650 mg, 60%) as an unstable yellowish oil, b.p. 118—121° at 0.1 mmHg; δ 1.2 (3 H, d, *J* 7.5 Hz), 1.85 (4 H, m), 3.35 (5 H, m), 4.9 (1 H, d, *J* 2.5), and 7.0—7.7 (4 H, complex).[13]

2-*Benzoyl*-3-*methylindan*-1-*one* (7).—In a preparation similar to the foregoing, involving the enamine (2) (3.0 g, 16.2 mmol), addition of methyl iodide was followed after 5 min by simultaneous addition at −20 °C of freshly distilled triethylamine (5.0 ml, 36 mmol) and benzoyl chloride (2.4 g, 17.1 mmol) under nitrogen. The temperature was then allowed to rise and the mixture was stirred for 18—20 h at 25 °C under nitrogen. A green oily precipitate was formed, which gradually turned to a yellow-orange solid. The mixture was poured into water (100 ml) and extracted thrice with ether. The dried and concentrated organic portion was mixed with sodium acetate (10 g), acetic acid (10 ml), and water (50 ml) and stirred for 5 min at reflux. The oily emulsion was cooled, diluted with water, and worked up as usual to afford an oil (3.8 g). Chromatography on silica with benzene–hexane furnished the diketone (7) (2.8 g, 69%) as an oil, which crystallised from pentane–ether, giving pale yellow needles (750 mg, 19%), m.p. 79—81°. Recrystallisation from pentane provided material (7) with m.p. 80—82°; $\nu_{max.}$ 1 700—1 600br cm^{-1} in CCl_4, 1 610 cm^{-1} in KBr; δ 1.1 (3 H, d, *J* 7 Hz), 4.25 (1 H, q, *J* 7), 7.5 (6 H, complex), and 7.8 (3 H, complex) (a second tautomer, indicated by a methyl doublet at δ 1.4, is present to the extent of *ca.* 15% in CCl_4 solution and about 25% in $CHCl_3$) (Found: C, 81.45; H, 5.6. Calc. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.65%).

3,5-*Dihydro*-3,5-*dimethyl*-4-*phenylindeno*[1,2-d]*pyrimidin*-2-*one* (8).—*N*-Methylurea (6.0 g, 81 mmol) and the diketone (7) (6.0 g, 24 mmol) were refluxed for 1 h in acetic acid (100 ml) with introduction of dry hydrogen chloride through a gas dispersion tube. The mixture was cooled, poured into water, and extracted thrice with ethyl acetate. The organic layer was washed with dilute aqueous sodium hydrogen carbonate and water, dried, and vacuum-concentrated to furnish an oil (7 g), which crystallised from ether–pentane

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to give the *pyrimidone* (8) (2.5 g, 36%), m.p. 227—230°. Recrystallisation from dichloromethane–pentane provided white prisms, m.p. 228—231° (decomp.); δ 0.9 (3 H, d, *J* 7 Hz), 3.4 (3 H, s), 3.95 (1 H, q, *J* 7), 7.2—7.7 (8 H, complex), and 8.1 (1 H, m) (Found: C, 79.4; H, 5.6; N, 9.4. $C_{19}H_{16}N_2O$ requires C, 79.1; H, 5.6; N, 9.7%).

3,3-*Dimethylindan*-1-*one* (11).—A solution of the enamine (2) (2.0 g, 10.8 mmol; freshly distilled) in dry THF (20 ml) was stirred at 25 °C under nitrogen during addition of n-butyl-lithium (1.6M in hexane; 7.5 ml, 12.0 mmol) in small portions. After 5—10 min stirring at 25 °C, the solution of the anion was cooled (ice-bath) and quenched with methyl iodide (0.78 ml, 12.5 mmol). The resulting mixture was stirred for 3 min at 25 °C, then more butyl-lithium (7.5 ml) was added and the mixture was heated gently at reflux for 5 min, cooled (ice-bath), and quenched with more methyl iodide (0.78 ml). After 5 min stirring, water (25 ml) was added and the mixture was stirred overnight under nitrogen. Vacuum concentration and the usual work-up provided a yellowish residue (1.9 g), which was distilled to furnish the ketone (11) (1.65 g, 95%) as an oil, b.p. 65—71° at 0.1 mmHg (lit.,[9] 115—117° at 18 mmHg); δ 1.35 (6 H, s), 2.45 (2 H, s), and 7.0—7.65 (4 H, complex). The 2,4-dinitrophenylhydrazone (70% yield) had m.p. 265—266° (lit.,[9,14] 266 and 270°).

2-(*Pyrrolidin*-1-*yl*)*indene* (13).—A mixture of indan-2-one (5.0 g, 37.8 mmol) and pyrrolidine (4.0 ml, 48 mmol) was refluxed for 2 h under nitrogen in benzene (150 ml) with azeotropic water separation. The mixture was vacuum-concentrated to one quarter of its volume and decolourised; addition of pentane furnished the enamine (5.5 g, 79%) as light brown plates, m.p. 105—107°. Although this m.p. is about 15° below the reported [8] value of 120—121°, this material was used successfully without further purification and n.m.r. indicated high purity: δ 1.85 (4 H, m), 3.1 (6 H, complex), 5.0 (1 H, s), and 6.45—7.1 (4 H, complex).

1-*Methylindan*-2-*one* (16).—A solution of the enamine (13) (3.0 g, 16.2 mmol) in dry THF (40 ml) was cooled to −65 °C and stirred under nitrogen during addition of n-butyl-lithium (1.6M in hexane; 12 ml, 19.2 mmol) in small portions. The resulting solution was stirred for 15 min at −65 °C, and then methyl iodide (1.2 ml, 19 mmol) was added. After an additional 5 min stirring at −65 °C, N-hydrochloric acid (20 ml) was added, THF was evaporated off *in vacuo*, water (50 ml) was added, and the mixture was refluxed for 5 min. The usual isolation procedure gave an oil (2.3 g), which was chromatographed on silica gel with pentane–benzene to provide the ketone (16) (1.9 g). Distillation afforded material (1.60 g, 68%) of b.p. 64—66° at 0.3 mmHg (lit.,[8] 140—143° at 3.5—3.7 mmHg), which g.l.c. indicated to contain about 5% of indan-2-one; $\nu_{max.}$ 1 760 cm^{-1}; δ 1.35 (3 H, d, *J* 7 Hz), 3.35 (1 H, q, *J* 7), 3.4 (2 H, s), and 7.2 (4 H, s). The 2,4-dinitrophenylhydrazone (62% yield) had m.p. 197—198° (decomp.) (lit.,[15] 184—185.5°) (from acetone–THF–pentane) (Found: C, 58.6; H, 4.4. Calc. for $C_{16}H_{14}N_4O_4$: C, 58.9; H, 4.3%).

Dimethylation of the enamine (13), carried out by using the amounts and procedures described for the dimethylation of (2), with hydrolysis by refluxing HOAc–NaOAc buffer solution, yielded (after distillation) a yellow oil (1.45 g, 84%), b.p. 72—78° at 0.1 mmHg. N.m.r. and g.l.c. suggested the presence of a mixture of (19) and (20) in the ratio 1 : 1.15—1 : 1.3, with no (12) and little (16), and with (20) probably present as a mixture of epimers.

1-*Benzoyl*-3-*methyl*-2-(*pyrrolidin*-1-*yl*)*indene* (17).—In a preparation similar to the foregoing monomethylation, involving the enamine (13) (3.0 g, 16.2 mmol), addition of methyl iodide was followed after 10 min by addition of freshly distilled triethylamine (5.0 ml, 36 mmol). The temperature was then raised to 0 °C, benzoyl chloride (2.0 ml, 17.1 mmol) was added, and the mixture was stirred for 48 h at 25 °C under nitrogen. The mixture was poured into water (100 ml) and extracted with several portions of ether. The extracts were dried and vacuum-concentrated providing an oil (5.2 g) which crystallised from ether–pentane to give the *benzoylenamine* (17) (2.5 g, 51%) as orange prisms, m.p. 133—136 °C. Recrystallisation from ether–pentane raised the m.p. to 144—145° (decomp.); $\nu_{max.}$ 1 620sh and 1 600 cm^{-1}; δ 1.5 (3 H, d, *J* 7 Hz), 1.85 (4 H, m), 3.35 (4 H, m), 3.7 (1 H, q, *J* 7), 6.55—7.35 (4 H, m), 7.5 (3 H, m), and 7.9 (2 H, m) (Found: C, 82.9; H, 7.05. $C_{21}H_{21}NO$ requires C, 83.15; H, 7.0%).

1,2-*Diphenyl*-4-(*pyrrolidin*-1-*yl*)*cyclopenta*-1,3-*diene* (22).—A mixture of the enone (21) [16] (10.0 g, 42.7 mmol), pyrrolidine (3.8 ml, 45.6 mmol), and toluene-*p*-sulphonic acid (50 mg) was refluxed for 18 h under nitrogen in benzene (150 ml) with azeotropic water separation. The residue obtained after vacuum-concentration crystallised on cooling and was triturated with cold ether, decolourised, and crystallised from ether–pentane to furnish the enamine (22) (8.7 g, 71%) as yellow-brown needles, m.p. 97—100°. Recrystallisation raised the m.p. to 98—101°; δ 1.9 (4 H, m), 3.15 (4 H, m), 3.4 (2 H, s), 4.95 (1 H, s), and 6.7—7.4 (10 H, complex).

2-*Methyl*-3,4-*diphenylcyclopent*-2-*enone* (25).—A solution of the enamine (22) (1.43 g, 5.0 mmol) in dry THF (15 ml) under nitrogen was cooled at −40 °C and stirred during addition of n-butyl-lithium (1.6M in hexane; 4.0 ml, 6.4 mmol). After 15 min stirring at −40 °C, methyl iodide (0.42 ml, 6.6 mmol) was added and stirring was continued for 5 min. The solution was then mixed with water (20 ml), acetic acid (6 ml), and sodium acetate (1.5 g) and heated for 1 h on a steam-bath. The usual work-up gave an oil, which was chromatographed on silica gel with benzene–chloroform to furnish an oil (850 mg), which crystallised from ether–pentane to afford the *ketone* (25) (630 mg, 51%) as tiny white nuggets, m.p. 68—71°. Recrystallisation raised the m.p. to 73.5—75.5° (lit.,[17] m.p. 74—75 and 77—78°); $\nu_{max.}$ 1 710 cm^{-1}; δ 1.9 (3 H, d, *J* 2 Hz), 2.3 (1 H, dd, *J* 2 and 19), 2.9 (1 H, dd, *J* 7 and 19), 4.35br (1 H), 7.05 (5 H, s), and 7.2 (5 H, s) [18] (Found: C, 87.4; H, 6.5. Calc. for $C_{18}H_{16}O$: C, 87.1; H, 6.5%).

5-*Acetyl*-2-*methyl*-3,4-*diphenylcyclopent*-2-*enone* (26).—In a preparation similar to the foregoing, involving the enamine (22) (1.43 g, 5.0 mmol), addition of methyl iodide was followed after 5 min by addition of freshly distilled triethylamine (1.0 ml, 7.2 mmol) and then acetyl chloride (0.35 ml, 5.0 mmol). The resulting emulsion was heated for 2 h at reflux, then poured into a mixture of water (20 ml), acetic acid (6 ml), and sodium acetate (1.5 g) and heated for 30

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min on a steam-bath. The usual work-up furnished an oil (1.4 g), which was filtered in benzene through a short column of silica gel and concentrated. The resulting oil was a mixture of two major components (t.l.c.), which were separated by chromatography on silica gel with pentane–benzene. The first component eluted was an oil (26) (530 mg, 37%) which yielded white *crystals* (220 mg, 15%) (from pentane), m.p. 103—105°; $\nu_{max.}$ 1 660 and 1 625 cm^{-1}; δ 1.65 (3 H, s), 1.95 (3 H, d, J 2 Hz), 4.6 (1 H, q, J 2), and 6.9—7.35 (10 H, complex) [18] (Found: C, 82.8; H, 6.3. $C_{20}H_{18}O_2$ requires C, 82.7; H, 6.3%).

Further elution gave the enone (25) (360 mg, 29%) as an oil which crystallised from pentane, yielding a solid (170 mg, 14%), m.p. 72—74°, identical with that previously prepared (by n.m.r., t.l.c., and mixed m.p.).

1-(3,4-*Diphenylcyclopenta*-1,3-*dienyl*)-1-*methylpyrrolidinium Iodide* (27).—A mixture of the enamine (22) (1.0 g, 3.5 mmol) and methyl iodide (1.0 g, 7.1 mmol) was refluxed under nitrogen in dry dioxan (15 ml) for 30 h with formation of a yellow precipitate. Water (10 ml) was then added and the mixture was refluxed for 1 h. Vacuum concentration and the usual work-up furnished an oil, which crystallised from chloroform–ether in yellow needles to give the *salt* (27) (650 mg, 43%), m.p. 251—252° (decomp.); $\nu_{max.}$ 1 680 cm^{-1}; *m/e* 301 (M − HI) and 287 (M − CH_3I) (Found: C, 61.2; H, 5.4; I, 29.1; N, 3.4. $C_{22}H_{24}IN$ requires C, 61.5; H, 5.6; I, 29.6; N, 3.3%), soluble in hot water, from which it can be recrystallised.

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